

The mutual co-implication of thermodynamics' first and second laws

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Abstract

In classical phenomenological thermodynamics the first and second laws can be regarded as independent statements. Statistical mechanics provides a microscopic substratum that explains thermodynamics in probabilistic terms via a microstate probability distribution $\{p_i\}$. We study here a hitherto unexplored microscopic connection between the two laws. Given an information measure (or entropic form), each of the two laws implies the other through the process $p_i \rightarrow p_i + dp_i$.

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1 Introduction

Macroscopically, in classical phenomenological thermodynamics, the first and second laws can be regarded as independent statements. In statistical mechanics an underlying microscopic substratum is added that is able to explain thermodynamics itself [1, 2, 3, 4].

Of this substratum, a microscopic probability distribution (PD) that controls the population of microstates is a basic ingredient [1]. Changes that affect exclusively microstate-population give rise to “heat” [2, 4]. How these changes are related to energy-changes provides the essential content of the first law [2].

In this effort we show that the above mentioned PD establishes a link between the first and second laws of thermodynamics, according to the following scheme:

- Given an entropic form (or an information measure (IM)) S , a mean energy U and a temperature T ,
- and for any system described by a microscopic probability distribution (PD) $\{p_i\}$,
- assuming a heat transfer process via $p_i \rightarrow p_i + dp_i$,
- 1) if the PD $\{p_i\}$ maximizes S this entails $dU = TdS$, and, alternatively,
- 2) if $dU = TdS$, this predetermines a unique PD that maximizes S .

Symbolically, given a specific IM,

$$dU = TdS \Leftrightarrow \text{MaxEnt prob. distr. } \{p_i\}.$$

2 From the second to the first law

A quite general treatment is given in, for instance [5, 6] (by no means an exhaustive list!). Here, for completeness’ sake, we provide a rudimentary sketch of the pertinent arguments.

One way to be sure that one complies with the strictures of the second law is to use MaxEnt [4], i.e., maximize the entropy S with, say M , appropriate constraints. If the pertinent microstates are denoted with the subindex i , and the physical quantity A_k , ($k = 1, \dots, M$) takes the value $A_k(i)$ at the microstate i , then the constraints read

$$\langle A_k \rangle = \sum_i p_i A_k(i); \quad (k = 1, \dots, M). \quad (1)$$

We will denote the Boltzmann constant by k_B and assume that $k = 1$ corresponds to the energy E with $(A_1(i) \equiv \epsilon_i)$, so that, in such a case the above expression specializes to

$$U \equiv \langle A_1 \rangle = \sum_i p_i \epsilon_i. \quad (2)$$

One should now maximize the “Lagrangian” Φ [4]

$$\Phi = S/k_B - \alpha \sum_i p_i - \beta \sum_i p_i \epsilon_i - \sum_{k=2}^M \lambda_k \sum_i p_i A_k(i), \quad (3)$$

in order to obtain the actual distribution $\{p_i\}$ from the equation

$$\delta_{p_i} \Phi = 0. \quad (4)$$

However, since in this paper we are interested just in the “heat” part we shall not consider the last term on the right-hand-side of (3). We argue that, if p_i changes to $p_i + dp_i$, because of (4) we have

$$0 = dS/k_B - \beta dU, \quad (5)$$

which implies (note that, because of normalization, $\sum_i \delta p_i = 0$), with $\beta = 1/k_B T$, T the temperature [2]

$$dU = T dS, \quad (6)$$

which concludes the argument [5] that MaxEnt leads to the first law.

The whole procedures given both in this and in the forthcoming Section can be repeated including also the *work* “ $\lambda_k A_k$ ”-terms of (3), of course. Such an extension is straightforward and we omit it for brevity’s sake.

3 From the first law to the second

Our *central goal* is to traverse now the opposite direction as that of the preceding Section. We shall start the present considerations by assuming that one deals with a rather *general* information measure of the form

$$S = k \sum_i p_i f(p_i), \quad (7)$$

where, for simplicity’s sake, Boltzmann’s constant is denoted now just by k . The sum runs over a set of quantum numbers, collectively denoted by i (characterizing levels of energy ϵ_i), that specify an appropriate basis in Hilbert’s space and $\mathcal{P} = \{p_i\}$ is an (as yet unknown) un-normalized probability distribution such that

$$\sum_i p_i = \text{constant}. \quad (8)$$

Finally, f is an arbitrary smooth function of the p_i . Further, we assume that mean values of quantities A that take the value A_i with probability p_i are evaluated according to

$$\langle A \rangle = \sum_i A_i g(p_i), \quad (9)$$

with g another arbitrary smooth function of the p_i . In particular, the mean energy U is given by

$$U = \sum_i \epsilon_i g(p_i). \quad (10)$$

Assume now that the set \mathcal{P} changes in the fashion

$$p_i \rightarrow p_i + dp_i, \text{ with } \sum_i dp_i = 0 \text{ (on account of (8))}, \quad (11)$$

which in turn generates corresponding changes dS and dU in, respectively, S and U . We are talking just about level-population changes, i.e., heat. We want then to make sure that the heat part of thermodynamics' first law is obeyed, so that we impose the condition that, in the above described circumstances,

$$dU - TdS = 0, \quad (12)$$

with T the temperature. As a consequence of (12), a little algebra yields, up to first order in the dp_i , the condition

$$\epsilon_i g'(p_i) - kT [f(p_i) + p_i f'(p_i)] = 0, \quad (13)$$

where the primes indicate derivative with respect to p_i . Eq. (13) should hopefully yield one and just one expression for the p_i . We proceed to show that this is indeed the case by examining below several important situations.

4 Shannon's entropy

Here we take

$$f(p_i) = -\ln(p_i), \text{ and } g(p_i) = p_i. \quad (14)$$

In these circumstances, Eq. (13) becomes

$$-\epsilon_i = kT[\ln(p_i) + 1], \quad (15)$$

which immediately yields (remember (11))

$$p_i = \frac{1}{e} \exp(-\epsilon_i/kT), \quad (16)$$

that after normalization yields the canonical Boltzmann distribution (BD). We conclude that this distribution is the only one that guarantees obedience to the first law for Shannon's information measure. A posteriori, one ascertains that the BD maximizes entropy as well, with U as a constraint, which establishes a link with the second law.

5 Tsallis measure with linear constraints

We have now, for any real number q [7, 8, 9],

$$f(p_i) = \frac{(1 - p_i^{q-1})}{q-1}, \quad \text{and} \quad g(p_i) = p_i, \quad (17)$$

so that $f'(p_i) = -p_i^{q-2}$ and Eq. (13) becomes, with $\beta = (1/kT)$,

$$qp_i^{q-1} = 1 - (q-1)\beta\epsilon_i, \quad (18)$$

which after normalization yields Tsallis' celebrated 1988 distribution

$$\begin{aligned} p_i &= Z_q^{-1} [1 - (q-1)\beta\epsilon_i]^{1/(q-1)} \\ Z_q &= \sum_i [1 - (q-1)\beta\epsilon_i]^{1/(q-1)}. \end{aligned} \quad (19)$$

6 Tsallis measure with non-linear constraints, un-normalized

The information measure is still the one built up with the function $f(p_i)$ of (17), but we use now the so-called Curado-Tsallis 1991 constraints [10] that arise if one uses

$$g(p_i) = p_i^q \Rightarrow g'(p_i) = qp_i^{q-1}. \quad (20)$$

Eq. (13) leads to

$$p_i = \left(\frac{1}{q}\right)^{1/(q-1)} [1 - (1-q)\beta\epsilon_i]^{1/(1-q)}, \quad (21)$$

and, after normalization, one is led to the Curado-Tsallis distribution [10]

$$\begin{aligned} p_i &= (Z_q)^{-1} [1 - (1-q)\beta\epsilon_i]^{1/(1-q)} \\ Z_q &= \sum_i [1 - (1-q)\beta\epsilon_i]^{1/(1-q)}. \end{aligned} \quad (22)$$

7 Tsallis measure with non-linear constraints, normalized

This is the standard treatment nowadays [7]. It was proposed in [11]. One has

$$g(p_i) = \frac{p_i^q}{w_q}; \quad w_q = \sum_i p_i^q; \quad U_q = \sum_i g(p_i) \epsilon_i, \quad (23)$$

which entails

$$g'(p_i) = \frac{qp_i^{q-1}}{w_q} [1 - \frac{p_i^q}{w_q}]. \quad (24)$$

This is to be inserted into (13) and one finds

$$(1-q)\beta\epsilon_i g'(p_i) = qp_i^{q-1} - 1 \quad (25)$$

i.e.,

$$qp_i^{q-1} = [1 + \frac{(1-q)\beta qp_i^{q-1}\epsilon_i}{w_q} (1 - \frac{p_i^q}{w_q})]. \quad (26)$$

Now, we see that qp_i^{q-1} is the common factor of the quantity \mathcal{C}

$$\mathcal{C} = 1 - \frac{(1-q)\beta\epsilon_i}{w_q} (1 - \frac{p_i^q}{w_q}) \Rightarrow qp_i^{q-1}\mathcal{C} = 1, \quad (27)$$

so that

$$\frac{1}{qp_i^{q-1}} = \mathcal{C} = \left[1 - (1-q)\beta \frac{\epsilon_i}{w_q} (1 - \frac{p_i^q}{w_q}) \right], \quad (28)$$

If in the equality above we sum over the running index i we get

$$\begin{aligned} \mathcal{S} &= \sum_i \frac{1}{qp_i^{q-1}} - \sum_i \left(\frac{(1-q)\beta}{w_q} \epsilon_i [1 - \frac{p_i^q}{w_q}] \right) \\ &\equiv \sum_i \frac{1}{qp_i^{q-1}} - \mathcal{S}_1 + \mathcal{S}_2 = 0, \end{aligned} \quad (29)$$

with

$$\begin{aligned} \mathcal{S}_1 &= \sum_i \frac{(1-q)\beta}{w_q} \epsilon_i \\ \mathcal{S}_2 &= \sum_i \frac{(1-q)\beta}{w_q} \epsilon_i \frac{p_i^q}{w_q}, \end{aligned} \quad (30)$$

Consider now \mathcal{S}_2 . It acquires the appearance

$$\mathcal{S}_2 = \frac{(1-q)\beta}{w_q} \sum_i \epsilon_i \frac{p_i^q}{w_q} = \frac{(1-q)\beta}{w_q} U_q, \quad (31)$$

i.e., it is a *constant* independent of i . Assume that, for the system one is interested in, the spectrum consists of \mathcal{N} nondegenerate energy levels i . One can then rearrange things in (31) so as to add together \mathcal{N} terms U_q in \mathcal{S}_2 , using the obvious trick $\mathcal{S}_2 = \mathcal{S}_2(\mathcal{N}/\mathcal{N})$, so that we have

$$-\mathcal{S}_1 + \mathcal{S}_2 = \sum_i^{\mathcal{N}} \left(\frac{(1-q)\beta}{w_q} [\epsilon_i - \frac{U_q}{\mathcal{N}}] \right). \quad (32)$$

Tsallis et al. [11] argue at this point that one is, of course, free to shift the energy scale so as to add a fixed amount $W = U_q \frac{\mathcal{N}-1}{\mathcal{N}}$ to each ϵ_i , according to the Mach's dictum: *no absolute origins*. Since the origin of the energy spectrum can always be freely chosen, one can legitimately assume then the *uniform* energy-shift

$$\epsilon_i \mapsto \varepsilon_i; \quad \varepsilon_i = \epsilon_i + U_q \frac{\mathcal{N}-1}{\mathcal{N}}.$$

This enables Tsallis et al. to write [11]

$$-\mathcal{S}_1 + \mathcal{S}_2 = \sum_i^{\mathcal{N}} \left(\frac{(1-q)\beta}{w_q} [\varepsilon_i - U_q] \right), \quad (33)$$

and argue that \mathcal{S} clearly vanishes if, in the first line of (29), that now reads

$$\mathcal{S} = \sum_i \frac{1}{qp_i^{q-1}} - \sum_i \left(\frac{(1-q)\beta}{w_q} [\varepsilon_i - U_q] \right), \quad (34)$$

each i -term vanishes by itself (with ϵ replaced by ε). This prompts one to write the pertinent, properly normalized probability distribution in the TMP fashion [11]

$$\begin{aligned} p_i &= Z_q^{-1} [1 - \frac{(1-q)\beta}{w_q} (\varepsilon_i - U_q)]^{1/(1-q)} \\ Z_q &= \sum_i \left[1 - \frac{(1-q)\beta}{w_q} (\varepsilon_i - U_q) \right]^{1/(1-q)}. \end{aligned} \quad (35)$$

8 Exponential entropic form

This is given in [6, 12] and also used in [13]. One has

$$f(p_i) = \frac{1 - \exp(-bp_i)}{p_i} - S_0, \quad (36)$$

where b is a positive constant and $S_0 = 1 - \exp(-b)$, together with

$$g(p_i) = \frac{1 - e^{-bp_i}}{S_0} \Rightarrow g'(p_i) = \frac{be^{-bp_i}}{S_0}, \quad (37)$$

which, inserted into (13), after a little algebra, leads to

$$p_i = \frac{1}{b} \left[\ln \frac{b}{S_0} + \ln \left(1 - \frac{\beta \epsilon_i}{S_0} \right) \right]. \quad (38)$$

which, after normalization, gives the correct answer [12].

9 Conclusion

We have endeavored to show in this communication that, from a microscopic perspective, the first and second law of thermodynamics co-imply themselves in reciprocal fashion, that is

- assuming entropy is maximum one immediately derives the first law, and
- if you assume the validity of the first law and an information measure, this predetermines a probability distribution that maximizes entropy.

The first item has been known for some time (see, for instance, [5, 6]). As far as we know, the present is the first instance in which the second item has received detailed discussion.

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